**ABSTRACT**

To provide a zincate zinc plating bath capable of efficiently forming a zinc plating film with high brightness and high qualities even at a low current density. The zincate zinc plating bath is used in electroplating for depositing a metal containing at least zinc and forming a zinc plating film. It contains a primary brightener having a function of reducing the size crystals of the metal to be deposited and a plating accelerator containing a heterocyclic compound having a predetermined structure such as 2,5-dimercapto-1,3,4-thiadiazole.

**HETEROCYCLIC COMPOUND (PLATING ACCELERATOR)**

**REGION WHERE REDUCTION REACTION IS LIKELY TO OCCUR AND ZINC METAL NUCLEUS IS LIKELY TO BE GENERATED**

\[
\text{Zn(OH)}_2^– \rightleftharpoons \text{Zn(OH)} + \text{OH}^–
\]

\[
\text{ZnOH} + e^- \rightarrow \text{Zn} + \text{OH}^–
\]
HETEROCYCLIC COMPOUND (PLATING ACCELERATOR)

REGION WHERE REDUCTION REACTION IS LIKELY TO OCCUR AND ZINC METAL NUCLEUS IS LIKELY TO BE GENERATED

Zn(OH)₂ → Zn(OH) + OH⁻

ZnOH + e⁻ → Zn + OH⁻

SURFACE TO BE TREATED

PLATING EFFICIENCY

CURRENT DENSITY
FIG. 3

THICKNESS OF ZINC PLATING FILM (μm)

THEORETICAL VALUE AND MEASURED VALUE OF CURRENT DENSITY AT CATHODE (A/dm²)

CURRENT DENSITY DISTRIBUTION
ZINCATE ZINC PLATING BATH

TECHNICAL FIELD

[0001] The present invention relates to a zincate zinc plating bath used for forming a zinc plating film on automotive steel plates, bolts, nuts, and the like by using electroplating.

BACKGROUND ART

[0002] Zinc plating films have been used widely for various ordinary things including automotive steel sheets and mechanical parts formed of a steel material such as bolts and nuts for the improvement of corrosion resistance. Zinc alloy plating films made of, for example, zinc-nickel alloy, zinc-iron alloy, or tin-zinc alloy have also been used widely to satisfy demands for the improvement of heat resistance or salt water resistance.

[0003] Zinc plating films are formed using electroplating which is performed by supplying an electric current while dipping a material to be plated in a plating bath, and thereby electrophilizing the material to be plated. Plating baths for forming a zinc plating film can be roughly classified into an alkaline bath and an acid bath. Examples of the alkaline bath include a cyanide bath and a zincate zinc plating bath, while those of the acid bath include a zinc chloride bath and a zinc sulfate bath. From these plating baths, a proper one is selected as needed, depending on the desired conditions such as hardness and brightness of a plating film, shape and size of a material to be plated, and the like.

[0004] Among them, the zincate zinc plating bath has been preferred and employed industrially because it does not use cyanide which will become a burden on effluent treatment, a simple bath composition facilitates control of it, and this plating bath can be used even for small stamping parts, bolts and nuts. Zinc plating films formed using a zincate zinc plating bath are however inferior in all aspects of performance, covering power, and structural uniformity compared to films formed using a cyanide bath which is a similar alkaline bath. Even though, the zincate zinc plating bath is very effective for forming a zinc plating film under an industrial environment and many improved baths have been developed conventionally (refer to, for example, Patent Document 1).

[0005] Patent Document 1 discloses a zincate zinc plating bath containing a bath-soluble quaternary ammonium polymer. This zincate zinc plating bath can be mentioned as one of the excellent baths developed in recent years. With this zincate zinc plating bath, a zinc plating film exhibiting uniform electrodeposition and having high brightness can be formed on long materials or materials having a complex shape which therefore differ in the magnitude of current density.

SUMMARY OF THE INVENTION

[0009] With a view to satisfying the above objects, the present inventors have carried out an extensive investigation of a variety of compounds that can be contained in a primary brightener, a plating accelerator, and a secondary brightener and completed the present invention. In short, the present invention provides a zincate zinc plating bath which will be described below.

[0010] [1] A zincate zinc plating bath for depositing a metal containing at least zinc to form a zinc plating film by using electroplating, containing a primary brightener having a function of reducing the size of crystals of the metal thus deposited and a plating accelerator containing a heterocyclic compound represented by the following chemical formula (I):

[Chemical formula 1]

[0011] (in the chemical formula (I), n stands for a natural number from 1 to 3, R1 and R2 may be the same or different and each represents hydrogen, CH3COOH, CH3CH2OH, or CH2=CH(OH)CH2Cl, and/or a derivative of the heterocyclic compound.

[0012] [2] The zincate zinc plating bath as described above in [1], wherein the heterocyclic compound and/or the derivative of the heterocyclic compound is contained in an amount of 0.01 g/l or greater but not greater than 1.0 g/l.

[0013] [3] The zincate zinc plating bath as described above in [1] or [2], wherein a water-soluble cationic macromolecular compound is contained as the primary brightener.

Prior Art Document

Patent Document


[0007] In the zincate zinc plating bath disclosed in Patent Document 1, however, uniform electrodeposition is improved by suppressing the plating efficiency at a high current portion when electroplating which causes a wide range of current density distribution is performed and thereby decreasing a difference in thickness of the zinc plating film between the high current portion and a low current portion. With this zincate zinc plating bath, a thin zinc plating film having a uniform thickness can therefore be formed. There is accordingly a demand for an effect that cannot be found from the above-described conventionally known zincate zinc plating bath. Described specifically, in electroplating causing a wide range of current density distribution, there is a demand for a zincate zinc plating bath capable of forming a zinc plating film which is entirely thick, exhibits high uniform electrodeposition, and has high brightness mainly by improving the plating efficiency at a low current density. When the plating efficiency is enhanced, the conventionally known zincate zinc plating bath has problems such as deterioration in uniform electrodeposition and throwing power.

[0008] With the above problems in view, an object of the present invention is to provide a zincate zinc plating bath capable of efficiently forming a zinc plating film even when electroplating is performed at a low current density. Described specifically, the object is to provide a zincate zinc plating bath having a high plating efficiency and high throwing power when electroplating is performed at a low current density. Another object is to provide, when electroplating which causes a wide range of current density distribution including a low current density (from 0.05 to 1.0 A/dm²) is performed, a zincate zinc plating bath capable of forming a thick zinc plating film and exhibiting highly uniform electrodeposition mainly by improving the plating efficiency at a low current density. A further object of the present invention is to provide a zincate zinc plating bath capable of forming a zinc plating film with high brightness and high qualities.
The zincate zinc plating bath as described above in [3], wherein a compound represented by the following chemical formula (II):

\[
\text{Chemical formula 2}
\]

The zincate zinc plating bath as described above in [4], wherein a compound represented by the following chemical formula (III) having a specific structure as the primary brightener and contains also a secondary brightener.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view showing adsorption of a heterocyclic compound contained as a plating accelerator to a surface to be plated.

FIG. 2 illustrates the relationship between current density and plating efficiency in the zincate zinc plating bath of the present invention and a conventionally known zincate zinc plating bath.

FIG. 3 illustrates the relationship between current density and thickness of the zinc plating film in the zincate zinc plating bath (Example 9) of the present invention.

MODEL FOR CARRYING OUT THE INVENTION

Embodiments of the present invention will next be described. The present invention is not limited to or by the following embodiments. Changes, modifications or improvements can be made without departing from the scope of the present invention.

1. Zinlete Zinc Plating Bath:

Outline of the Zinlete Zinc Plating Bath of the Present Invention:

The zincate zinc plating bath of the present invention (which will hereinafter be called “plating bath of the present invention”) is for depositing a metal containing at least zinc to form a zinc plating film by using electroplating. The plating bath of the present invention is a zincate zinc plating bath containing a primary brightener having a function of reducing the size of crystals of a metal to be deposited, a plating accelerator containing a heterocyclic compound represented by the below chemical formula (I) and/or a derivative of the heterocyclic compound. The plating bath of the present invention can further contain a secondary brightener having a function of planarizing the zinc plating film.

Chemical formula 3

The zincate zinc plating bath as described above in any of [1] to [9], containing at least one of nickel ions or iron ions.

The zincate zinc plating bath as described above in [10], wherein the nickel ions are contained in an amount of 100 mg/L or greater but not greater than 4000 mg/L.

The zincate zinc plating bath as described above in [10] or [11], wherein the iron ions are contained in an amount of 10 mg/L or greater but not greater than 150 mg/L.

The zincate zinc plating bath of the present invention enables efficient formation of a zinc plating film. Described specifically, it exhibits a high plating efficiency and a high throwing power when electroplating is performed at a low current density. In addition, when electroplating is performed at a wide range of current densities including a low current density (from 0.05 to 1.0 A/dm²), the zincate zinc plating bath of the present invention exhibits highly uniform electrodeposition and enables the formation of a thick zinc plating film mainly by improving the plating efficiency at a low current density. Further, the zincate zinc plating bath of the present invention enables the formation of a zinc plating film with high brightness and high qualities when it contains a water soluble cationic macromolecular compound (represented by the below-described chemical formula (III)) having a specific structure as the primary brightener and contains also a secondary brightener.

Chemical formula 3

[In the chemical formula (I), n stands for a natural number from 1 to 3, R¹ and R² may be same or different and each represents hydrogen, methyl, ethyl, isopropyl, 2-hydroxyethyl-CH₂CH₂(OCH₂CH₂)OH (X standing for a natural number from 0 to 6), or 2-hydroxyethyl-CH₂CH₂(OCH₂CH₂)OH (X standing for a natural number from 0 to 6), R³ represents (CH₂)₂—O—(CH₂)₂, (CH₂)₂—O—(CH₂)₂—O—(CH₂)₂, or CH₂—CHOH—CH₂—O—CH₂—CHOH—CH₂, and Y represents S or O) as contained as the water soluble cationic macromolecular compound.

[In the chemical formula (II), n stands for a natural number of 1 or greater, R¹, R², R³, and R⁴ may be the same or different and each represents hydrogen, methyl, ethyl, isopropyl, 2-hydroxyethyl-CH₂CH₂(OCH₂CH₂)OH (X standing for a natural number from 0 to 6), or 2-hydroxyethyl-CH₂CH₂(OCH₂CH₂)OH (X standing for a natural number from 0 to 6), R³ represents (CH₂)₂—O—(CH₂)₂, (CH₂)₂—O—(CH₂)₂—O—(CH₂)₂, or CH₂—CHOH—CH₂—O—CH₂—CHOH—CH₂, and Y represents S or O) as contained as the water soluble cationic macromolecular compound.

[In the chemical formula (III), n stands for a natural number from 1 to 3, R¹ and R² may be the same or different and each represents hydrogen, CH₂COOH, CH₂CH₂OH, or CH₂CH(OH)CH₂Cl].

The term “primary brightener” as used herein is similar to an agent which is called “primary brightener”, carrier, stress inhibitor, or the like by those skilled in the plating field. The primary brightener has a function of reducing the size of crystals of a metal thus deposited to form a smooth zinc plating film and also has a function of relaxing an internal stress of the zinc plating film. The term “secondary brightener” as used herein is similar to an agent called “secondary brightener”, “leveler”, or the like by those
skilled in the plating field. The secondary brightener has a planarizing effect on a zinc plating film when the zinc plating film is formed by electroplating.

[0034] These primary and secondary brighteners have, as these terms suggest, a function of forming a zinc plating film with brightness. In particular, using the primary brightener and the secondary brightener in combination can accelerate reduction of the size of a deposited metal and give a mirror surface brightness to the zinc plating film. In the plating bath of the present invention, a compound contained in the primary brightener and the secondary brightener can be selected, depending on the appearance of the zinc plating film such as matte plating, half-brightness plating, brightness plating (which will be described later in detail).

[0035] The term “plating accelerator” as used herein means an additive having a deposition accelerating action which is added for plating by those skilled in the plating field. The plating accelerator is a substance accelerating an electrode reaction of plating and increasing a current density. Incidentally, in this specification, a plating film containing zinc as a main metal component is collectively called “zinc plating film” and when a plating film containing an alloy of zinc and another metal as the component thereof should be called in distinction from the zinc plating film, a description will be made, while calling it “zinc alloy plating film” (for example, Zn—Ni alloy plating film).

[0036] The plating bath of the present invention enables the efficient formation of a zinc plating film even when electroplating is performed in a low current region and further enables the formation of a zinc plating film with high brightness and high qualities under predetermined conditions. The plating bath of the present invention exhibits highly uniform electrodeposition, high throwing power, and high plating efficiency even when electroplating is performed in a low current region. The plating bath of the present invention can therefore be used effectively for barrel plating in which electroplating is usually performed in a low current region (which will be described later in detail).

[0037] Components of the plating bath of the present invention will next be described. First, zinc and alkali used as “essential components” will be described and then, “plating accelerator”, “primary brightener”, and “secondary brightener” will be described in detail successively.

[0038] 1-2. Essential Components of the Plating Bath of the Present Invention

[0039] The plating bath of the present invention contains, similar to the conventionally known zincate zinc plating bath, zincate zinc ([Zn(OH)]_2^-). The zincate zinc can be prepared by using, as needed, the method ordinarily employed by those skilled in the plating technology. For example, to obtain a plating bath having zincate zinc dissolved therein, it is recommended to prepare zincate zinc by dissolving zinc oxide (ZnO) in an aqueous alkaline solution such as an aqueous sodium hydroxide (NaOH) solution similar to the conventionally known method.

[0040] The plating bath of the present invention contains zinc ions preferably in an amount of 5 g/L or greater but not greater than 20 g/L from the standpoint of practical use of a zinc plating film relating to the qualities thereof (appearance, film thickness, ease of after treatment, corrosion resistance). Amounts of zinc ions contained in the plating bath less than 5 g/L are not preferred because they deteriorate appearance of the zinc plating film and deteriorate corrosion resistance due to a decrease in the thickness of the zinc plating film. Amounts of zinc ions contained in the plating bath exceeding 20 g/L, on the other hand, are not preferred because they cause poor appearance of the zinc plating film or deterioration in a throwing power. As the amount of zinc ions contained in the plating bath, an amount of zinc ions (Zn^{2+}) determined by conversion of the mass of raw materials such as zinc oxide (ZnO) in terms of a molecular weight can be used.

[0041] The plating bath of the present invention contains sodium hydroxide (NaOH) preferably in an amount of 80 g/L or greater but not greater than 250 g/L from the standpoint of stability of the plating bath and practical use of a zinc plating film relating to the qualities thereof (appearance, film thickness, ease of after treatment, corrosion resistance). Amounts of sodium hydroxide contained in the plating bath less than 80 g/L are not preferred because the plating bath loses its stability and causes poor appearance of the zinc plating film or deterioration in throwing power. Amounts of sodium hydroxide contained in the plating bath exceeding 250 g/L, on the other hand, are not preferred because a too high concentration of sodium hydroxide is not suited for practical use.

[0042] 1-3. Plating Accelerator

[0043] The plating accelerator to be contained in the plating bath of the present invention contains a heterocyclic compound represented by the above chemical formula (I) and/or a derivative of the heterocyclic compound. The term “derivative of the heterocyclic compound represented by the above chemical formula (I)” as used herein means a derivative of a 1,3,4-thiadiazole. Specific examples of the compound represented by the above chemical formula (I) and derivatives thereof include 2,5-dimercapto-1,3,4-thiadiazole, 2-thionoctic acid-5-mercapto-1,3,4-thiadiazole, 2-(dithioacetic acid)-1,3,4-thiadiazole, 2-hydroxyethylthio-5-mercapto-1,3,4-thiadiazole, 2-hydroxyethylthio-5-mercapto-1,3,4-thiadiazole, 2-thionoctic acid-5-mercapto-1,3,4-thiadiazole, and epichlorohydrin-modified 2,5-dimercapto-1,3,4-thiadiazole.

[0044] In FIG. 1, 2,5-dimercapto-1,3,4-thiadiazole is used as an example of the heterocyclic compound represented by the above chemical formula (I) or derivative thereof and it schematically illustrates an assumed adsorption state of 2,5-dimercapto-1,3,4-thiadiazole to a surface to be plated. As illustrated in FIG. 1, sulfur atoms constituting two substituents and a 5-membered ring chemically adsorb to the surface to be plated. It is presumed that deposition of a metal such as zinc is accelerated because a reduction reaction is likely to occur in a space, represented by a dotted pattern in FIG. 1, between the sulfur atoms constituting two substituents and 5-membered ring and the surface to be plated. The above-described derivatives of the heterocyclic compound represented by the chemical formula (I) embrace compounds having a molecular structure of a compound in which chemical adsorption is shown schematically in FIG. 1 is presumed to occur and available by adding a substituent or carrying out a skeleton change based on the heterocyclic compound represented by the above chemical formula (I) without departing from the range permitting those skilled in the field of plating technology or organic chemistry to design.

[0045] The plating bath of the present invention contains the heterocyclic compound represented by the above chemical formula (I) and/or derivative thereof preferably in an amount of from 0.01 g/L or greater but not greater than 1.0 g/L from the standpoint of improving the plating efficiency.

[0046] The above-described heterocyclic compounds represented by the above formula (I), derivatives thereof, and compounds prepared based on these compounds greatly contribute to an improvement in plating efficiency when electro-
plating is performed using the plating bath of the present invention. In addition, these heterocyclic compounds and derivatives thereof serve to bestow high brightness, in other words, give high brightness to a zinc plating film formed using the plating bath of the present invention.

[0047] 1-4. Primary Brightener:

[0048] The plating bath of the present invention contains a primary brightener. Examples of the primary brightener to be contained in the plating bath of the present invention include anionic surfactants, nonionic surfactants, and water soluble macromolecular organic compounds such as polyeckylene polyamines, each generally used for various zinc plating baths as a primary brightener. Particularly in the plating bath of the present invention, primary brighteners containing a water soluble cationic macromolecular compound are preferred.

[0049] Examples of the water soluble cationic macromolecular compound include polyallylamines, polylyamide polyamines, polyepeoxy polyamines, and polyalkylene polyamines. The polyallylamines include a polydiallyldimethylammonium chloride—sulfur dioxide copolymer. The polyepeoxy polyamines include a condensation polymer of ethylenediamine and epichlorohydin, a condensation polymer of dimethyldiminopropylamine and epichlorohydin, a condensation polymer of imidazole and epichlorohydin, a condensation polymer of an imidazole derivative such as 1-methylimidazole or 2-methylimidazole and epichlorohydin, and a condensation polymer of a heterocyclic amine including a triazine derivative such as acetoguanamine or benzoguanamine and epichlorohydin. The polylyamide polyamines include polyamine polystyrene resins, more specifically, a condensation polymer of 3-dimethylaminopropylurea and epichlorohydin and a condensation polymer of bis[N,N-dimethyldiminopropyl]urea and epichlorohydin and water soluble nylon resins, more specifically, a condensation polymer of N,N-dimethyldiminopropylamine, alkylenedi-carboxylic acid, and epichlorohydin. The polyeckylene polyamines include diethynlenetriamine, triethynlenetetramine, tetraethynlenepentamine, hexaethynlenepentamine, a condensation polymer of dimethyldimino propylamine and 2,2'-dichlorodiethyl ether, a condensation polymer of dimethyldimino propylamine and 1,3-dichloropropene, a condensation polymer of N,N,N',N'-tetramethyl-1,3-diaminopropene and 2,2'-dichlorodi ethyl ether, a condensation polymer of N,N,N',N'-tetramethyl-1,3-diaminopropene and 1,4-dichlorobutane, and a condensation polymer of N,N,N',N'-tetramethyl-1,3-diaminopropene and 1,3-dichloropropene-2-ol.

[0050] In particular, the primary brightener contained in the plating bath of the present invention more preferably contains, as the water soluble cationic macromolecular compound, a compound represented by the following chemical formula (II) from the standpoint of improving the uniform electrodeposition and throwing power.

![Chemical formula II]

[0051] In the chemical formula (II), n stands for a natural number of 1 or greater, R, R, R, and R may be the same or different and each represents hydrogen, methyl, ethyl, isopropyl, 2-hydroxyethyl-CH₂CH₂(OH)CH₂CH₂OH(X stands for a natural number from 0 to 6), or 2-hydroxyethyl-CH₂CH₂(OH)CH₂CH₂OH (X stands for a natural number from 0 to 6), R represents (CH₂)ₙ-O-(CH₂)₂, (CH₂)ₙ-O-(CH₂)₂, or (CH₂)ₙ-O-(CH₂)₂, or CH₃-CO-(CH₂)₇ or CH₃-CO-(CH₂)₇ or CH₃-CO-(CH₂)₇ or CH₃-CO-(CH₂)₇ or Y represents S or O).

[0052] 1-5: Secondary Brightener:

[0053] The plating bath of the present invention optionally contains a secondary brightener. Examples of the secondary brightener include those containing an organic aldehyde and/or a heterocyclic compound.

[0054] Particularly from the standpoint of improving the brightness and improving the throwing power, the secondary brightener to be used in the plating bath of the present invention preferably contains at least either one of an aromatic aldehyde or a pyridinium compound.

[0055] Examples of the aromatic aldehyde preferably contained as the secondary brightener in the plating bath of the present invention include anisaldehyde, veratraldehyde, salicylaldehyde, vanillin, piperonal, and p-hydroxybenzaldehyde. In particular, the aromatic aldehyde contained as the secondary brightener to be used in the plating bath of the present invention is more preferably veratraldehyde and vanillin from the standpoint of improvement of brightness and stability of the compound to be contained in the zinc plating bath.

[0056] Examples of the pyridinium compound preferably contained as the secondary brightener in the plating bath of the present invention include benzyl pyridinium carboxylate (3-carboxybenzyl pyridinium chloride) and 3-carbamoylbenzyl pyridinium chloride.

[0057] 2. Embodiment for Forming a Zinc Alloy Plating Film

[0058] The plating bath of the present invention can be used not only for a zinc plating film composed mainly of zinc but also for the formation of a zinc alloy plating film such as zinc-nickel alloy (which will hereinafter be called “Zn—Ni alloy”), zinc-iron alloy (which will hereinafter be called “Zn—Fe alloy”), and zinc-iron-nickel alloy (which will hereinafter be called “Zn—Fe—Ni alloy”) by electroplating. Incidentally, when nickel ions functioning also as a metal brightener are incorporated in the plating bath of the present invention, a zinc plating film (Zn—Ni alloy film or Zn—Fe—Ni alloy film) having a good brightness appearance can sometimes be formed without the secondary brightener (refer to Example 8 which will be described later).

[0059] In the plating bath of the present invention, nickel ions may be incorporated for the formation of a Zn—Ni alloy plating film; iron ions may be incorporated for the formation of a Zn—Fe alloy plating film; and iron ions and nickel ions may be incorporated for the formation of a Zn—Fe—Ni alloy plating film. When the nickel ions are incorporated in the plating bath of the present invention, it is possible to dissolve, for example, NiSO₄·6H₂O, NiCl₂·6H₂O, Ni(OH)₂, or the like in the plating bath. When iron ions are incorporated in the plating bath of the present invention, it is possible to dissolve, for example, Fe₂(SO₄)₃·7H₂O, FeSO₄·7H₂O, Fe(OH)₃, FeCl₃·6H₂O, FeCl₂·4H₂O, or the like.

[0060] When the plating bath of the present invention contains nickel ions, an amount of nickel ions is preferably 100 mg/L or greater but not greater than 4000 mg/L from the
standpoint of improving the qualities of the zinc plating film (appearance, film thickness, ease of after treatment, corrosion resistance). When the plating bath contains the nickel ions in an amount less than 100 mg/L or exceeding 4000 mg/L, a zinc plating film superior in desired appearance, ease of after treatment, ease of chemical conversion treatment, corrosion resistance, or heat resistance cannot be obtained.

[0061] When the plating bath of the present invention contains iron ions, an amount of iron ions is preferably from 10 mg/L or greater but not greater than 150 mg/L from the standpoint of improving the quality of the zinc plating film (appearance, film thickness, ease of after treatment, corrosion resistance). When the plating bath contains iron ions in an amount less than 10 mg/L or exceeding 150 mg/L, a zinc plating film superior in desired appearance, ease of after treatment, ease of chemical conversion treatment, corrosion resistance, or heat resistance cannot be obtained.

[0062] In the embodiment for forming a zinc alloy plating film, incorporation of a chelating agent in the plating bath of the present invention is preferred. As this chelating agent, a primary brightener also functioning as a chelating agent such as diethylenetriamine or triethylenetetramine may be employed. In the embodiment for forming a zinc alloy plating film having, as a component thereof, nickel, iron, or both of them, the plating bath of the present invention contains, as a chelating agent, preferably tartaric acid, citric acid, gluconic acid, ethylenediamine, hexamine, 1,2-diamino propane, 1,3-
diaminopropane, 1,2-diaminobutane, 1,4-diaminobutane, tri-aminothiylamine, methyaminopropanolamine, monoethanolamine, diethanolamine, triethanolamine, diethanolaminopropylamine, 2-hydroxyethylaminopropylamine, 1,3-bis(3-amino propoxy)ethane, nitrotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentacetic acid (DTPA), triethylenetetramine-
hexacetic acid (TTHA), or the like.

[0063] 3. Action/Effect of the Zincate Zinc Plating Bath of the Present Invention:

[0064] FIG. 2 shows the relationship between current density and plating efficiency when electroplating causing a wide range of current density distribution is performed with the conventionally known zincate zinc plating bath (including known improved ones prior to the present patent application) and the zincate zinc plating bath of the present invention. First, the conventional zincate zinc plating bath has a high plating efficiency at a high current density, while it has a low plating efficiency at a low current density (a broken line A in FIG. 2). Such variations in plating efficiency due to a difference in the magnitude of current density occurs because deposition of zinc is accelerated only at a high current density. In addition, zinc ions are consumed at a position of a high current density and sufficient zinc ions for deposition cannot be ensured at a position of a low current density. This increases the variation in plating efficiency due to a difference in the magnitude of current density. In an improved zincate zinc plating bath which is known prior to the present patent application and contains a water soluble cationic macromolecular compound represented by the below chemical formula (III) as a primary brightener, the plating efficiency at a high current density is suppressed by reducing the current efficiency at a high current density. Thus, in the above improved zincate zinc plating bath, a difference in plating efficiency between a high current density and a low current density decreases and uniform electrodeposition is improved, but an average plating efficiency is low and a zinc plating film thus formed is thin (a broken line B in FIG. 2). In the plating bath of the present invention, a plating efficiency at a low current density is enhanced (a solid line C in FIG. 2, for details, refer to Evaluation test 4 in Example which will be described later). This improvement in plating efficiency at a low current density is mainly caused by improvement in uniform electrodeposition in the plating bath of the present invention. With the plating bath of the present invention, an average plating efficiency is high and a thick and uniform zinc plating film can be formed (for details, refer to Evaluation test 3 in Example which will be described later).

EXAMPLES

[0065] The present invention will hereinafter be described in further detail based on Examples. It should however be noted that the present invention is not limited to or by them.

[0066] 4. Preparation of Zincate Zinc Plating Bath:

[0067] 4-1. For Zinc Plating Film Having Only Zinc as a Metal Component:

Example 1

[0068] In accordance with the composition shown in Table 1, a zincate zinc plating bath containing 8 g/L of zinc ions, 10 g/L of sodium hydroxide, 0.4 g/L of a 1:1 (molar ratio) condensation polymer of dimethylamino propylamine and epichlorohydrin (Compound A of Table 1, product of URSA CHEMIE GMBH, Product number: Product J 138 M) as a primary brightener, 0.03 g/L of veratraldehyde—Na sulfate adduct (product of Wako Pure Chemical Industries, which will equally apply hereinafter) as a secondary brightener obtained by dissolving and reacting in a sodium hydrogen sulfite solution, and 0.05 g/L of 2,5-dimercapto-1,3,4-thiadiazole (Compound J in Table 1, product of Toyo Chemical Industry, MTD) as a plating accelerator, was prepared. The concentration of each of the above compounds (including a polymer) was adjusted by conversion in terms of a purity (content) and a molecular weight of a commercially available product of each compound obtained (which will equally apply to determination of the concentration of a compound of another commercially available product).

### TABLE 1

<table>
<thead>
<tr>
<th>Example</th>
<th>Zinc ions (g/L)</th>
<th>Nickel ions (g/L)</th>
<th>Sodium hydroxide (g/L)</th>
<th>Primary brightener Kind*1</th>
<th>Secondary brightener Kind*</th>
<th>Benzyl pyridinium carboxylate (g/L)</th>
<th>Plating accelerator Kind*</th>
</tr>
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<tbody>
<tr>
<td>Example 1</td>
<td>8</td>
<td>0</td>
<td>100</td>
<td>A [0.4]</td>
<td>A</td>
<td>0</td>
<td>J [0.050]</td>
</tr>
<tr>
<td>Example 2</td>
<td>6</td>
<td>0</td>
<td>100</td>
<td>B [1.0]</td>
<td>B</td>
<td>0.025</td>
<td>J [0.020]</td>
</tr>
<tr>
<td>Example 3</td>
<td>9</td>
<td>0</td>
<td>120</td>
<td>B [0.6]</td>
<td>B</td>
<td>0</td>
<td>J [0.075]</td>
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TABLE 1-continued

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<tr>
<th>Example 4</th>
<th>Example 5</th>
<th>Example 6</th>
<th>Example 7</th>
<th>Example 8</th>
<th>Example 9</th>
<th>Example 10</th>
<th>Example 11</th>
<th>Example 12</th>
<th>Example 13</th>
<th>Comp. Ex. 1</th>
<th>Comp. Ex. 2</th>
<th>Comp. Ex. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc ions (g/L)</td>
<td>12</td>
<td>15</td>
<td>12</td>
<td>13</td>
<td>11</td>
<td>10</td>
<td>18</td>
<td>16</td>
<td>13</td>
<td>12</td>
<td>8</td>
<td>10</td>
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<tr>
<td>Nickel ions (g/L)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Sodium hydroxide (g/L)</td>
<td>120</td>
<td>115</td>
<td>125</td>
<td>130</td>
<td>125</td>
<td>100</td>
<td>140</td>
<td>140</td>
<td>130</td>
<td>120</td>
<td>100</td>
<td>140</td>
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<tr>
<td>Concentration (g/L)</td>
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<td>0.050</td>
<td>0.0</td>
<td>0.03</td>
<td>0.0</td>
<td>0.03</td>
<td>0.09</td>
<td>0.03</td>
<td>0.09</td>
<td>0.09</td>
<td>0.08</td>
<td>0.03</td>
</tr>
<tr>
<td>Secondary brightener Kind *1</td>
<td>Benzyl</td>
<td>Anisaldehyde</td>
<td>Veratraldehyde</td>
<td>Benzyl</td>
<td>Anisaldehyde</td>
<td>Veratraldehyde</td>
<td>Benzyl</td>
<td>Anisaldehyde</td>
<td>Veratraldehyde</td>
<td>Benzyl</td>
<td>Anisaldehyde</td>
<td>Veratraldehyde</td>
</tr>
<tr>
<td>Concentration (g/L)</td>
<td></td>
<td>0.03</td>
<td>0.0</td>
<td>0.0</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*1: A to D represent the following compounds:
A: condensation polymer of dimethylaminopropylamine and epichlorohydrin
B: compound represented by the chemical formula (III) (MIRAPOL WT)
C: poly(dimethylaminoethyl)ammonium chloride/sulfur dioxide copolymer
D: 1:2 (molar ratio) condensation polymer of ethylenediamine and epichlorohydrin
E: tris(2-aminomethyl)ammonium
F: a 1:0.73 (molar ratio) condensation polymer of imidazole and epichlorohydrin (containing about 18% of an imidazole component)
G: a 1:1 (molar ratio) condensation polymer of imidazole and epichlorohydrin (containing about 38% of an imidazole component)
H: a 1:0.73 (molar ratio) condensation polymer of 1-methylimidazole and epichlorohydrin (containing about 21% of a 1-methylimidazole component)
I: a 1:1 (molar ratio) condensation polymer of 2-methylimidazole and epichlorohydrin (containing about 21% of a 2-methylimidazole component)
J: 2,5-dimercapto-1,3,4-thiadiazole
K: 2-chloroacetic acid-5-mesappto-1,3,4-thiadiazole
L: 2-hydroxyethylsulfonic-5-mesappto-1,3,4-thiadiazole
M: epichlorohydrin-modified 2,5-dimercapto-1,3,4-thiadiazole
*2: It contains 1.2 (g/L) of Compound A as described above in *1 and 1.0 (g/L) of Compound F as a primary brightener (this also applies to Examples 11 to 13, and Comparative Example 5).

Example 2

[0069] In accordance with the composition shown in Table 1, a zincate zinc plating bath containing 6 g/L of zinc ions, 100 g/L of sodium hydroxide, 1.0 g/L of a water soluble cationic macromolecular compound represented by the below-described formula (III) (Compound B of Table 1, trade name: MIRAPOL (trade mark) WT, product of Rhodia [formerly Rhone-Poulenc], CAS No. 68555-36-2) as a primary brightener, 0.025 g/L of anisaldehyde-Na sulfate adduct (product of Wako Pure Chemical Industries, which will equally apply hereinafter) as a secondary brightener obtained by dissolving and reacting in a sodium hydroxide sulfate solution, and 0.02 g/L of 2,5-dimercapto-1,3,4-thiadiazole (Compound J of Table 1) as a plating accelerator was prepared.

Example 3

[0070] In accordance with the composition shown in Table 1, a zincate zinc plating bath containing 9 g/L zinc ions, 120 g/L of sodium hydroxide, 0.6 g/L of a water soluble cationic macromolecular compound represented by the above chemical formula (III) (Compound B of Table 1, trade name: MIRAPOL (trade mark) WT, product of Rhodia, CAS No. 68555-36-2) as a primary brightener, 0.050 g/L of anisaldehyde-Na sulfate adduct as a secondary brightener, and 0.075 g/L of 2,5-dimercapto-1,3,4-thiadiazole (Compound J of Table 1) as a plating accelerator was prepared.

Example 4

[0071] In accordance with the composition shown in Table 1, a zincate zinc plating bath containing 12 g/L of zinc ions, 120 g/L of sodium hydroxide, 1.0 g/L of a water soluble cationic macromolecular compound represented by the above-described formula (III) (Compound B of Table 1, trade name: MIRAPOL (trade mark) WT, product of Rhodia, CAS No. 68555-36-2) as a primary brightener, 0.025 g/L of veratraldehyde as a secondary brightener, and 0.075 g/L of 2,5-dimercapto-1,3,4-thiadiazole (Compound J of Table 1) as a plating accelerator was prepared.

Example 5

[0072] In accordance with the composition shown in Table 1, a zincate zinc plating bath containing 15 g/L of zinc ions, 135 g/L of sodium hydroxide, 1.5 g/L of a water soluble cationic macromolecular compound represented by the above-described formula (III) (Compound B of Table 1, trade name: MIRAPOL (trade mark) WT, product of Rhodia, CAS No. 68555-36-2) as a primary brightener, 0.050 g/L of anisaldehyde-Na sulfate adduct as a secondary brightener,
and 0.200 g/L of 2,5-dimercapto-1,3,4-thiadiazole (Compound J of Table 1) as a plating accelerator was prepared.

Example 6

[0073] In accordance with the composition shown in Table 1, a zincate zinc plating bath containing 12 g/L of zinc ions, 125 g/L of sodium hydroxide, 0.4 g/L of polydiallyldimethylammonium chloride/sulfur dioxide copolymer (Compound C of Table 1, trade name: diallyldimethylammonium chloride—sulfur dioxide copolymer [quaternary amine/SO₂], product of Nitto Boseki, Product No: PAS-A-5 as a primary brightener, 0.06 g/L of benzyl pyridinium carboxylate (benzyl pyridinium carboxylate aqueous solution, Lugulvan BPC-48, product of BASF) as a secondary brightener, and 0.050 g/L of 2,5-dimercapto-1,3,4-thiadiazole (Compound J of Table 1) as a plating accelerator was prepared.

Example 7

[0074] In accordance with the composition shown in Table 1, a zincate zinc plating bath containing 15 g/L of zinc ions, 130 g/L of sodium hydroxide, 1.5 g/L of a condensation polymer obtained by reacting ethylene dine and epichlorohydrin at a molar ratio of 1.2 (Compound D of Table 1, product of URSA CHEMIE GMBH, product No: Product JF 220) as a primary brightener, 0.03 g/L of a veratraldehyde—Na sulfite adduct as a secondary brightener, and 0.100 g/L of 2,5-dimercapto-1,3,4-thiadiazole (Compound J of Table 1) as a plating accelerator was prepared.

Example 8

[0075] In accordance with the composition shown in Table 1, a zincate zinc plating bath containing 10 g/L of zinc ions, 100 g/L of sodium hydroxide, 1.0 g/L of a water soluble cationic macromolecular compound represented by the above chemical formula (III) (Compound B of Table 1, trade name: MIRAPOL (trade mark) WT, product of Rhodia, CAS No. 68555-36-2) as a primary brightener, 0.03 g/L of an anisaldehyde—Na sulfite adduct as a secondary brightener, and 0.060 g/L of 2,5-dimercapto-1,3,4-thiadiazole (Compound J of Table 1) as a plating accelerator was prepared.

Example 9

[0076] In accordance with the composition shown in Table 1, a zincate zinc plating bath containing 18 g/L of zinc ions, 140 g/L of sodium hydroxide, 1.2 g/L of a water soluble cationic macromolecular compound represented by the above chemical formula (III) (Compound B of Table 1, trade name: MIRAPOL (trade mark) WT, product of Rhodia, CAS No. 68555-36-2) and 1.0 g/L, in terms of a solid content, of a condensation polymer obtained by reacting imidazole and epichlorohydrin at a molar ratio of 1:0.73 (containing approximately 18% of the imidazole component) (Compound F of Table 1) as a primary brightener, 0.09 g/L of an anisaldehyde—Na sulfite adduct as a secondary brightener, and 0.050 g/L of 2,5-dimercapto-1,3,4-thiadiazole (Compound J of Table 1) as a plating accelerator was prepared.

Example 10

[0077] In accordance with the composition shown in Table 1, a zincate zinc plating bath containing 16 g/L of zinc ions, 140 g/L of sodium hydroxide, 0.6 g/L of a water soluble cationic macromolecular compound represented by the above chemical formula (III) (Compound B of Table 1, trade name: MIRAPOL (trade mark) WT, product of Rhodia, CAS No. 68555-36-2) and 1.5 g/L of a condensation polymer obtained by reacting imidazole and epichlorohydrin at a molar ratio of 1:1 (containing approximately 18% of the imidazole component) (Compound G of Table 1) as a primary brightener, 0.03 g/L of an anisaldehyde—Na sulfite adduct as a secondary brightener, and 0.100 g/L of 2-(thiocetacetic acid)-5-mercaptop-1,3,4-thiadiazole (Compound K of Table 1) as a plating accelerator was prepared.

Example 11

[0078] In accordance with the composition shown in Table 1, a zincate zinc plating bath containing 13 g/L of zinc ions, 130 g/L of sodium hydroxide, 1.2 g/L of a water soluble cationic macromolecular compound represented by the above chemical formula (III) (Compound B of Table 1, trade name: MIRAPOL (trade mark) WT, product of Rhodia, CAS No. 68555-36-2) and 0.15 g/L of a condensation polymer obtained by reacting 1-methylimidazolide (product of Nippon Synthetic Chemical Industry, 1MI) and epichlorohydrin at a molar ratio of 1:0.73 (containing approximately 21% of the 1-methylimidazolide component) (Compound H of Table 1) as a primary brightener, 0.03 g/L of an aqueous solution of benzyl pyridinium carboxylate (benzyl pyridinium carboxylate aqueous solution, Lugulvan BPC-48) as a secondary brightener, and 0.075 g/L of 2-hydroxyethylthio-5-mercaptop-1,3,4-thiadiazole (Compound L of Table 1) as a plating accelerator was prepared.

Example 12

[0079] In accordance with the composition shown in Table 1, a zincate zinc plating bath containing 12 g/L of zinc ions, 120 g/L of sodium hydroxide, 1.2 g/L of a water soluble cationic macromolecular compound represented by the above chemical formula (III) (Compound B of Table 1, trade name: MIRAPOL (trade mark) WT, product of Rhodia, CAS No. 68555-36-2) and 0.5 g/L of a condensation polymer obtained by reacting 2-methylimidazolide (product of Nippon Synthetic Chemical Industry, 2MI) and epichlorohydrin at a molar ratio of 1:1 (containing approximately 21% of the 2-methylimidazole component) (Compound I of Table 1) as a primary brightener, 0.09 g/L of an anisaldehyde—Na sulfite adduct as a secondary brightener, and 0.20 g/L of epichlorohydrin-modified 2,5-dimercapto-1,3,4-thiadiazole (Compound M of Table 1) as a plating accelerator was prepared.

Comparative Example 1

[0080] In accordance with the composition shown in Table 1, a zincate zinc plating bath containing 8 g/L of zinc ions, 100 g/L of sodium hydroxide, 1.0 g/L of a 1:1 (molar ratio) condensation polymer of dimethylaminopropylamine and epichlorohydrin (Compound A of Table 1, product of URSA CHEMIE GMBH, product No: Product J 138 M) as a primary brightener, and 0.05 g/L of an anisaldehyde—Na sulfite adduct as a secondary brightener was prepared.

Comparative Example 2

[0081] In accordance with the composition shown in Table 1, a zincate zinc plating bath containing 19 g/L of zinc ions, 100 g/L of sodium hydroxide, 1.0 g/L of a water soluble cationic macromolecular compound represented by the above chemical formula (III) (Compound B of Table 1, trade name: MIRAPOL (trade mark) WT, product of Rhodia, CAS No.
68555-36-2) as a primary brightener, and 0.03 g/L of an anisaldehyde—Na sulfite adduct as a secondary brightener was prepared.

Comparative Example 3

[0082] In accordance with the composition shown in Table 1, a zincate zinc plating bath containing 14 g/L of zinc ions, 140 g/L of sodium hydroxide, 1.2 g/L of a water soluble cationic macromolecular compound represented by the above chemical formula (III) (Compound B of Table 1, trade name: MIRAPOL, trade mark WT, product of Rhodia, CAS No. 68555-36-2) and 0.75 g/L of a condensation polymer obtained by reacting imidazole and epichlorohydrin at a molar ratio of 1:0.73 (containing approximately 18% of the imidazole component) (Compound F of Table 1) as a primary brightener, and 0.08 g/L of an anisaldehyde—Na sulfite adduct as a secondary brightener was prepared.

[0083] Example 8

[0084] In accordance with the composition shown in Table 1, a zincate zinc plating bath containing 11 g/L of zinc ions, 2.25 g/L of nickel ions, 120 g/L of sodium hydroxide, 30 g/L of tetraethylenepentamine (Compound E of Table 1) as a primary brightener, and 0.08 g/L of 2,5-dimercapto-1,3,4-thiadiazole (Compound J of Table 1) as a plating accelerator was prepared.

[0085] 5. Evaluation Test of Zincate Zinc Plating Bath:

[0086] Using the zincate zinc plating baths of Examples 1 to 13 and Comparative Examples 1 to 3, electroplating was performed in accordance with each evaluation item described below and the plating films thus formed were evaluated.

[0087] 5-1. Evaluation Test (Evaluation Test 1) of Brightness Appearance, Peeling, and Blister of a Zinc Plating Film Formed by Electroplating Causing a Wide Range of Current Density Distribution Including a Current Density Region (from 0.05 to 2.5 A/dm²);

[0088] 5-1-1: Electroplating:

[0089] Each of the plating baths of Examples 1 to 13 and Comparative Examples 1 to 3 was placed in an circulating type hull cell (trade name: Smart Hull Cell, product of Yamamoto MS, product No: B-53-SM) equipped with a stir having a rotation speed of 1000 rpm and electroplating was performed. As an anode and a cathode for the formation of a zinc plating film, an iron sheet of 45 mm long, 45 mm wide, and 1 mm thick and an iron sheet of 67 mm long, 100 mm wide, and 0.3 mm thick made by Yamamoto MS were used, respectively. Electroplating was performed under the following conditions: current of 0.5 A (current density of from 0.05 to 2.5 A/dm²), current carrying time of 60 minutes, and electroplating bath temperature of 25°C.

[0090] Table 2 shows the results of the evaluation test conducted for visually judging the brightness of the zinc plating films obtained using the zincate zinc plating baths of Examples 1 to 13 and Comparative Examples 1 to 3. As a result of comparison between Example 2 and Comparative Example 2 which are contrast examples from the standpoint of the presence or absence of 2,5-dimercapto-1,3,4-thiadiazole (Compound J of Table 1) contained as a plating accelerator, the zinc-plating film formed in Example 2 has an entire brightness, while the zinc-plating film formed in Comparative Example 2 has a semi-brightness. This suggests that 2,5-dimercapto-1,3,4-thiadiazole contained as a plating accelerator acts to improve the brightness of the zinc plating film. Similarly, 2-thioacetic acid)-5-mercapto-1,3,4-thiadiazole (Compound K of Table 1) contained in Example 11, 2-thiophenylthio-5-mercapto-1,3,4-thiadiazole (Compound L of Table 1) contained in Example 12, and epichlorohydrin-modified 2,5-dimercapto-1,3,4-thiadiazole (Compound M of Table 1) contained in Example 13, such as a plating accelerator, also acts to improve the brightness of the respective zinc plating films thus obtained. The term “entire brightness” in Table 2 means that a plating film has substantially a uniform mirror surface. The term “brightness” in Table 2 means that a plating film has an entire brightness but the brightness is a little dull. The term “semi-brightness” means that a plating film has more dull brightness. The term “entire white” means that a plating film has a uniformly matte surface.

<table>
<thead>
<tr>
<th>Evaluation test 1</th>
<th>Evaluation test 2</th>
<th>Evaluation test 3</th>
<th>Evaluation test 4</th>
<th>Uniform electrodeposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brightness</td>
<td>Peeling blister</td>
<td>Blackness brightness</td>
<td>Plating efficiency (mg A - min)</td>
<td>A percentage to the plating efficiency of Comp. Ex. 1 (%)</td>
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<td>Entire brightness</td>
<td>None</td>
<td>Good</td>
<td>89.3</td>
</tr>
<tr>
<td>Example 2</td>
<td>Entire brightness</td>
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<td>Good</td>
<td>87.3</td>
</tr>
<tr>
<td>Example 3</td>
<td>Entire brightness</td>
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<td>Good</td>
<td>95.3</td>
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<tr>
<td>Example 4</td>
<td>Entire brightness</td>
<td>None</td>
<td>Good</td>
<td>92.8</td>
</tr>
<tr>
<td>Example 5</td>
<td>Brightness</td>
<td>None</td>
<td>Good</td>
<td>84.3</td>
</tr>
<tr>
<td>Example 6</td>
<td>Semi-brightness</td>
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<td>Lack of brightness</td>
<td>92.3</td>
</tr>
<tr>
<td>Example 7</td>
<td>Entire white</td>
<td>None</td>
<td>Lack of brightness</td>
<td>87.0</td>
</tr>
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<td>Example 8</td>
<td>Entire brightness</td>
<td>None</td>
<td>Good</td>
<td>—</td>
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<td>Example 9</td>
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<td>None</td>
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<td>92.8</td>
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<td>Comp. Ex. 3</td>
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<td>None</td>
<td>Lack of brightness</td>
<td>82.0</td>
</tr>
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</table>
5-1-3. Results of Evaluation Test of Peeling and Blister and Evaluation:

For the evaluation test of peeling and blister of a zinc plating film, rightly after electroplating using the above-described circulating type hull cell, the plated materials obtained using the plating baths of Examples and Comparative Examples were each heat treated at 60°C for 72 hours. Table 2 shows the results of the evaluation test conducted by visually confirming the presence or absence, after the heat treatment, of peeling and blister of the zinc plating films formed using the zincate zinc plating baths of Examples 1 to 13 and Comparative Examples 1 to 3. Neither peeling nor blister was observed from the heat-treated zinc plating films obtained using the baths of these Examples and Comparative Examples.

Incidentally, a zinc plating film was formed even on the surface of the iron sheet of the cathode, which was on the opposite side to a surface facing the anode, as a result of electroplating using the zincate zinc plating baths of Examples 1 to 13. This fact has revealed that the zincate zinc plating baths of Examples 1 to 13 have an excellent throwing power even for forming a zinc plating film by utilizing a very faint current leaked to the reverse side of the iron sheet of the cathode.

5-2. Evaluation Test on the Brightness and the Like of a Plating Film Obtained by Subjecting the Zinc Plating Film Formed Using a Barrell Plating to Chemical Conversion Treatment (Evaluation Test 2):

Each of the zincate zinc plating baths of Examples 1 to 13 and Comparative Examples 1 to 3 was placed in a minbarrel (diameter [9] of a drum length [L]: 110 mm x 150 mm) and 1 kg of a hexagon bolt made of iron having a size, in accordance with JIS standards, of M10 was subjected to barrell plating at a current of 5A and a current carrying time of 50 minutes. After the barrell plating, the plated product was heat treated at 200°C for 3 hours and then allowed to cool, followed by chemical conversion treatment at 35°C for 45 seconds at pH 2.2 with a trivalent chromium black chemical conversion treatment agent (trade name: Metasu YTFB-SA/ SB, product of Yukan Industry). Then, the plated product was subjected to finishing treatment with a finishing treatment agent (trade name: Metasu CR-U3/12, product of Yukan Industry) and then dried at 80°C for 20 minutes. Thus, barrell plating was performed with each of the zincate zinc plating baths of Examples 1 to 13 and Comparative Examples 1 to 3, followed by chemical conversion treatment to form zinc plating films (hereinafter called “chemical conversion treatment zinc plating film”).

5-2-2. Results and Evaluation:

Table 2 shows the results of the evaluation test by which blackness and brightness of the chemical conversion treatment zinc plating films obtained using the zincate zinc plating baths of Examples 1 to 13 and Comparative Examples 1 to 3 were confirmed visually. The chemical conversion treatment zinc plating films formed in Examples 1 to 5 and Examples 8 to 13 showed good results in blackness and brightness. The chemical conversion treatment zinc plating films formed in Examples 6 and 7 showed good results in blackness, but their brightness was not sufficiently good (the definition of “brightness not sufficiently good” will be described later). The chemical conversion treatment zinc plating film formed in Comparative Example 1, which is a contrast example of Example 1 from the standpoint of presence or absence of 2,5-dimercapto-1,3,4-thiadiazole (Compound J of Table 1) contained as a plating accelerator, caused a trace defect due to generation of a gas. The chemical conversion treatment zinc plating film formed in Comparative Example 2, which is a contrast example of Example 2 from the standpoint of a plating accelerator, showed good results in blackness but it lacked brightness. It has therefore been elucidated from the results of Examples 1 to 5 and 8 to 13 that in the practical embodiment using barrel plating and conversion treatment in combination, the zincate zinc plating baths containing Compounds J, K, L, and M of Table 1, respectively, as a plating accelerator have also an enhancing action of qualities (appearance, ease of after treatment) of a zinc plating film. Incidentally, the term “good results in blackness” in this evaluation test means that the zinc plating film is jet black. The term “good results in brightness” in this evaluation test means that the zinc plating film has a gloss. The term “brightness not sufficiently good” in this evaluation test means that the zinc plating film lacks brightness and is smoky. The term “gas trace defect” in this evaluation test means that the zinc plating film has a white flow trace due to generation of a hydrogen gas.

5-3. Evaluation Test on the Relationship Between Current Density Distribution and Thickness of Zinc Plating Film (Evaluation Test 3):

5-3-1: Electroplating

The plating bath of Example 9 was placed in an circulating type hull cell (trade name: Smart Hull Cell, product of Yamamoto MS, product No: B-53-SM) equipped with a stir having a rotation speed of 1000 rpm and electroplating was performed. As an anode and a cathode for the formation of a zinc plating film, an iron sheet of 45 mm long, 45 mm wide, and 1 mm thick and an iron sheet of 67 mm long, 100 mm wide, and 0.3 mm thick made by Yamamoto MS were used, respectively. Electroplating was performed under the following conditions: current of 1.0 A, current carrying time of 15 minutes, and electroplating bath temperature of 30°C.

5-3-2: Measurement of Thickness of Zinc Plating Film:

Thicknesses of the zinc plating film at five positions, that is, 10 mm, 40 mm, 60 mm, 80 mm, and 90 mm from the end of the high current portion toward the end of the low current portion at the center of the plated surface of the hull cell cathode sheet were measured using a fluorescent X-ray coating thickness gauge (product of SII, SFT-9200). These positions correspond to 5.0 A/dm², 2.0 A/dm², 1.0 A/dm², 0.33 A/dm², and 0.1 A/dm², respectively, in primary current distribution theoretically derived from the electroplating conditions at a current of 1.0 A in the above-described hull cell form.

5-3-3. Results and Evaluation:

FIG. 3 shows the relationship between the current density distribution and the thickness of a zinc plating film. In FIG. 3, the theoretically derived current density distribution is indicated by a blank circle (⊙) and the thickness of the zinc plating film derived theoretically from this theoretic value of the current density is indicated by a blank triangle (△). In FIG. 3, a solid line indicates a film thickness and a broken line indicates a current density. In FIG. 3, measured values of the thickness of the zinc plating film in the present test using the plating bath of Example 9 is plotted with a solid triangle. The thicknesses of the zinc plating film at the points where the theorectical current densities were 0.5 A/dm², 2.0 A/dm², 1.0
A/dm², 0.33 A/dm², and 0.1 A/dm², respectively were all around 6 μm. This suggests that a uniform and thick zinc plating film can be formed using the plating bath of Example 9 even in electroplating causing a current density distribution as wide as from 0.1 to 5.0 A/dm². The results also show that a uniform and thick zinc plating film is formed even by carrying out electroplating for a current carrying time as short as 15 minutes in the plating bath of Example 9. Incidentally, when a conventionally known zincate plating bath is used, a zinc plating film having an average thickness of at most approximately from 3 to 4 μm can be formed even a current carrying time is increased (data is not shown). In the present test using the plating bath of Example 9, the average current density calculated from the measured film thickness was as low as 1.5 A/dm² (plotted with a solid square (■) in Fig. 3). Refer to Evaluation Test 4 with regards to the evaluation of plating efficiency at an average current density (1.0 A/dm²).

[0107] 5-4. Evaluation Test on Plating Efficiency at Average Current Density (1.0 A/dm²) (Evaluation Test 4):

[0108] 5-4-1. Electroplating:

[0109] Zinc plating films were formed on 0.25 dm² in total of both surfaces of a cold rolled steel plate (SPCC) 50 mm long, 25 mm wide, and 0.5 mm thick by electroplating using the zincate zinc plating baths of Examples 1 to 7 and 9 to 13, and Comparative Examples 1 to 3. The electroplating was performed under the conditions of average current density of 1.0 A/dm², current carrying time of 20 minutes, and plating bath temperature of 25°C.

[0110] 5-4-2. Calculation of Plating Efficiency:

[0111] The zinc plating films formed using the zincate zinc plating baths of Examples 1 to 7 and 9 to 13, and Comparative Examples 1 to 3 were each dissolved completely in dilute hydrochloric acid to prepare an analysis sample. The analysis sample was subjected to IPC analysis to find the zinc concentration therein. Based on the zinc concentration of the analysis sample, a zinc content in the zinc plating film, that is, a deposition amount of zinc due to electroplating was calculated. 2 plating efficiency (mg/A/min) was determined by dividing the zinc deposition amount of each of the zinc plating films formed using the plating baths of Examples 1 to 7 and 9 to 13, and Comparative Examples 1 to 3 by a current and current carrying time of electroplating.

[0112] 5-4-3. Results and Evaluation:

[0113] Table 2 shows the results of the evaluation test of the plating baths of Examples 1 to 7 and 9 to 13, and Comparative Examples 1 to 3 on plating efficiency and a ratio (percentage) to the plating efficiency of Comparative Example 1. As a result of a comparison between Example 1 and Comparative Example 1, Example 2 or 9 and Comparative Example 2, and Example 10 and Comparative Example 3, which are each a contrasting pair from the standpoint of the presence or absence of 2,5-dimercapto-1,3,4-thiadiazole (Compound J of Table 1) contained in a plating accelerator, a baths of Examples 1, 2, 9, and 10 containing 2,5-dimercapto-1,3,4-thiadiazole as a plating accelerator exhibit a better plating efficiency than those of Comparative Examples 1 to 3. In particular, the baths of Examples 1 to 7 and 9 to 13 containing Compound J, K, L, or M shown in Table 1 as a plating accelerator showed a plating efficiency as high as 84 or greater. It has therefore been elucidated that 2,5-dimercapto-1,3,4-thiadiazole contained as a plating accelerator is effective for enhancing the plating efficiency at a current density of 1.5 A/dm² or less.

[0114] Examples 1 to 7, 9, and 10 using 2,5-dimercapto-1,3,4-thiadiazole (Compound J of Table 1), Example 11 using 2-(thioacetic acid)-5-mercapto-1,3,4-thiadiazole (Compound K of Table 1), Example 12 using 2-hydroxyethylthio-5-mercapto-1,3,4-thiadiazole (Compound L of Table 1), and Example 13 using epichlorohydrin-modified 2,5-dimercapto-1,3,4-thiadiazole (Compound M of Table 1), each as a plating accelerator, showed a significant increase, that is, a 16 to 31% increase in plating efficiency compared with that of Comparative Example 1.

[0115] In plating baths containing a water soluble cationic macromolecular compound (MIRAPOL (trade mark) WT) represented by the above formula (III) at a low average current density of 1.0 A/dm², the 16 to 31% plating-efficiency increase brought by the plating baths of Examples 1 to 7 and 9 to 13 is very significant compared with the 7% and 13% plating-efficiency increases brought by the plating baths of Comparative Examples 2 and 3 belonging to the conventional art.

[0116] 5-5. Evaluation Test (Evaluation Test 5) on Uniform Electrodeposition:

[0117] 5-5-1: Electroplating:

[0118] The plating baths of Examples 1 to 7 and 9 to 13, and Comparative Examples 1 to 3 were each placed in an circulating type hull cell (trade name: Smart Hull Cell, product of Yamamoto MS, product No: B-53-SM) equipped with a stir having a rotation speed of 1000 rpm and electroplating was performed. As a cathode, an iron sheet 67 mm long, 100 mm wide, and 0.3 mm thick made by Yamamoto MS was used. Electroplating was performed under the following conditions: current of 0.5 A (current density from 0.05 to 2.5 A/dm², current carrying time of 60 minutes, and plating bath temperature of 25°C.

[0119] 5-5-2. Measurement of Thickness of Zinc Plating Film:

[0120] The thickness of the zinc plating film was measured at below-described two points of the above iron sheet used as the cathode. The position which was on the surface of the iron sheet, at the center of the surface to be plated in a depth direction of a plating cell when it was placed in a hull cell (plating cell), and which was 10 mm from a high current density end toward a low current density end was designated as Measuring point A. The position which was on the same surface of the same iron sheet, at the same depth as Measuring point A, and which was 85 mm from a high current density end toward a low current density end was designated as Measuring point B. The thicknesses of the zinc plating films at Measuring points A and B were measured using a fluorescent X-ray film thickness gauge (SFT-9200, product of SII). Uniform electrodeposition was determined as a ratio (percentage) of the film thickness of the zinc plating film at Measuring point B to that at Measuring point A.

[0121] 5-5-3. Results and Evaluation:

[0122] Table 2 shows the results of the evaluation test on uniform electrodeposition of the zincate zinc plating baths of Examples 1 to 7 and 9 to 13, and Comparative Examples 1 to 3. Example 1 and Comparative Example 1 and Example 2 and Comparative Example 2 which form a contrasting pair from the standpoint of the presence or absence of 2,5-dimercapto-1,3,4-thiadiazole (Compound J of Table 1) contained in the plating accelerator are examined. The value of uniform electrodeposition determined by the above calculation method is 47.9 in Example 1, while it is 30.7 in Comparative Example 1. Similarly, the value of uniform electrodeposition is 66.3 in
Example 2, while it is 60.8 in Comparative Example 2. Comparison of them has revealed that a zincate zinc plating bath containing 2,5-dimercapto-1,3,4-thiadiazole in a plating accelerator exhibits improved uniform electrodeposition.

[0123] The plating baths of Examples 2 to 5 and 9 to 13 and Comparative Example 2 containing a water soluble cationic macromolecular compound (MIRAPOL (trade mark) WT) represented by the above chemical formula (III) as a primary brightener exhibited uniform electrodeposition as high as 60 or greater. This result has revealed that the water soluble cationic macromolecular compound (MIRAPOL (trade mark) WT) represented by the above chemical formula (III) contained as a primary brightener is significantly effective for the improvement of uniform electrodeposition. The plating baths of Examples 2 to 5 and 9 to 13 containing any of Compounds J to M of Table 1 as a plating accelerator exhibited higher uniform electrodeposition. It has therefore been elucidated that the above plating accelerators are effective for improving uniform electrodeposition further. In particular, the plating baths of Examples 10 to 13 using the water soluble cationic macromolecular compound (MIRAPOL (trade mark) WT) represented by the above chemical formula (III) and a condensation polymer of imidazole and epichlorohydrin (any of Compounds F to I of Table 1) in combination and containing any of Compounds J to M of Table 1 as a plating accelerator showed uniform electrodeposition as high as 67 to 80.

[0124] 5.6 Synthetic Evaluation:

[0125] The above evaluation results have experimentally shown that the plating baths of Examples 1 to 13, that is, the plating baths of the present invention enable the formation of a zinc plating film having high brightness at a high plating efficiency even in electroplating at a low average current density (form 0.05 to 1.0 A/cm²). The zincate zinc plating baths of Examples 2 to 5 and 9 to 13 are embodiments of the plating bath of the present invention containing, as a plating accelerator, at least any one of Compounds J to M of Table 1 corresponding to the heterocyclic compound represented by the chemical formula (I) and a water soluble cationic macromolecular compound (MIRAPOL (trade mark) WT) represented by the above chemical formula (III) as a primary brightener. It has been shown experimentally that the above-mentioned plating baths show high uniform electrodeposition in addition to a high plating efficiency at a low average current density. It has also been shown experimentally that the zincate zinc plating baths of Examples 1 to 5 and 8 to 13 are effective for forming a zinc plating film excellent in qualities (appearance, ease of after treatment) even in practical embodiments using a barrel plating for 60-minute current carrying time and the chemical conversion treatment in combination.

INDUSTRIAL APPLICABILITY

[0126] The present invention can be used as a zincate zinc plating bath for forming a zinc plating film on automotive steel sheets, bolts, nuts, and the like by using electroplating.

1-12. (canceled)

13. A zincate zinc plating bath for depositing a metal containing at least zinc to form a zinc plating film by using electroplating, comprising a primary brightener having a function of reducing the size of crystals of the metal thus deposited and a plating accelerator containing a heterocyclic compound represented by the following chemical formula (I):

[Chemical formula 1]

\[
\begin{align*}
\text{S} & \quad \text{S} \\
R' & \quad R^2 \\
\end{align*}
\]

(in the chemical formula (I), n stands for a natural number from 1 to 3, R' and R^2 may be the same or different and each represents hydrogen, CH₂COOH, CH₃CH₂OH, or CH₃CH(OH)CH₂Cl and/or a derivative of the heterocyclic compound.

14. The zincate zinc plating bath according to claim 13, wherein the heterocyclic compound and/or the derivative of the heterocyclic compound is contained in an amount of 0.01 g/L or greater but not greater than 1 g/L.

15. The zincate zinc plating bath according to claim 13, wherein a water soluble cationic macromolecular compound is contained as the primary brightener.

16. The zincate zinc plating bath according to claim 14, wherein a water soluble cationic macromolecular compound is contained as the primary brightener.

17. The zincate zinc plating bath according to claim 15, wherein a compound represented by the following chemical formula (II):

[Chemical formula 2]

\[
\begin{align*}
\text{N} & \quad \text{C} \\
\text{N} & \quad \text{N} \\
\text{CH₂} & \quad \text{H} \\
\text{CH₂} & \quad \text{H} \\
\text{CH₂} & \quad \text{H} \\
\end{align*}
\]

(2nCl)

\[
\begin{align*}
\text{R'} & \quad \text{R}^2 \\
\text{R} & \quad \text{R}^4 \\
\end{align*}
\]

(in the chemical formula (II), n stands for a natural number of 1 or greater, R', R^2, R, and R^4 may be the same or different and each represents hydrogen, methyl, ethyl, isopropyl, 2-hydroxyethyl-CH₂CH₂OH (X stands for a natural number from 0 to 6), or 2-hydroxyethyl-CH₂CH₂CH₂(OCH₂CH₂)₆OH (X stands for a natural number from 0 to 6), R² represents (CH₃)₂O—(CH₂)₂, (CH₂)₂O—(CH₂)₆, or CH₃—CH₂OH—CH₂—O—CH₂—CHOH—CH₂, and Y represents S or O) is contained as the water soluble cationic macromolecular compound.

18. The zincate zinc plating bath according to claim 16, wherein a compound represented by the following chemical formula (II):

[Chemical formula 2]

\[
\begin{align*}
\text{N} & \quad \text{C} \\
\text{N} & \quad \text{N} \\
\text{CH₂} & \quad \text{H} \\
\text{CH₂} & \quad \text{H} \\
\text{CH₂} & \quad \text{H} \\
\end{align*}
\]

(2nCl)

\[
\begin{align*}
\text{R'} & \quad \text{R}^2 \\
\text{R} & \quad \text{R}^4 \\
\end{align*}
\]

(in the chemical formula (II), n stands for a natural number of 1 or greater, R', R^2, R, and R^4 may be the same or different
and each represents hydrogen, methyl, ethyl, isopropyl, 2-hydroxyethyl-CH₂CH₂(OCH₂CH₂)₂OH (X stands for a natural number from 0 to 6), or 2-hydroxyethyl-CH₂CH₂(OCH₂CH₂)₂OH (X stands for a natural number from 0 to 6). R² represents (CH₃)₂—O—(CH₂)₃, (CH₃)₂—O—(CH₂)₅, or CH₂—CHOH—CH₂—O—CH₂—CHOH—CH₂, and Y represents S or O is contained as the water soluble cationic macromolecular compound.

19. The zincate zinc plating bath according to claim 13, further comprising a secondary brightener having a function of planarizing the zinc plating film.

20. The zincate zinc plating bath according to claim 14, further comprising a secondary brightener having a function of planarizing the zinc plating film.

21. The zincate zinc plating bath according to claim 15, further comprising a secondary brightener having a function of planarizing the zinc plating film.

22. The zincate zinc plating bath according to claim 16, further comprising a secondary brightener having a function of planarizing the zinc plating film.

23. The zincate zinc plating bath according to claim 17, further comprising a secondary brightener having a function of planarizing the zinc plating film.

24. The zincate zinc plating bath according to claim 18, further comprising a secondary brightener having a function of planarizing the zinc plating film.

25. The zincate zinc plating bath according to claim 19, wherein at least one compound selected from the group consisting of organic aldehydes and heterocyclic compounds is contained as the secondary brightener.

26. The zincate zinc plating bath according to claim 25, wherein at least one of aromatic aldehyde or a pyridinium compound is contained as the secondary brightener.

27. The zincate zinc plating bath according to claim 13, comprising zinc ions in an amount of 5 g/L or greater but not greater than 20 g/L.

28. The zincate zinc plating bath according to claim 13, comprising sodium hydroxide in an amount of 80 g/L or greater but not greater than 250 g/L.

29. The zincate zinc plating bath according to claim 13, comprising at least one of either nickel or iron ions.

30. The zincate zinc plating bath according to claim 29, wherein the nickel ions are contained in an amount of 100 mg/L or greater but not greater than 4000 mg/L.

31. The zincate zinc plating bath according to claim 29, wherein the iron ions are contained in an amount of 10 mg/L or greater but not greater than 150 mg/L.

* * * * *